

Comparison of Absorption and Desorption of Cryomill Process Control Agents and Their Effect on Compressive Behavior of Trimodal Aluminum Metal-Matrix-Composites

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14. ABSTRACT Aluminum composite (AA5083) and boron carbide (B ₄ C) powders were cryomilled in liquid nitrogen using different process control agents (PCAs) such as oleic acid, caprylic acid, and stearic acid individually in order to determine the effect of each PCA on the resultant microstructure and mechanical properties. The microstructure of the powders was examined and consolidated samples were mechanically tested in compression. Chemical analysis was performed to determine impurity concentrations of nitrogen, hydrogen, and oxygen. Microstructural analysis of the powders revealed three types of agglomerates: composite powders of AA5083 with uniformly distributed B ₄ C particulate, unmilled spherical AA5083 powder and deformed AA5083 powder. These three types of agglomerates were found in similar size and proportion regardless of the PCA used. Correlation among PCA type, impurity concentrations, microstructure, and mechanical properties were examined.					
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1. Introduction

The U.S. Army is continuously looking for lightweight materials with high strength and high toughness for a variety of structural and survivability applications. It has been shown that a lightweight metal matrix composite (MMC) exhibits an excellent combination of specific stiffness and specific strength (*1*). The MMC consists of a high-strength nano-grained matrix of AA5083 (an aluminum alloy with approximately 4 wt.% Mg, <1 wt.% Mn and Cr combined), reinforced with high-modulus boron carbide (B_4C) ceramic particles blended with high-toughness AA5083 coarse-grained regions (*1, 2*). The unique multiscale microstructure of the MMC consisting of coarse grain (CG; average grain size approximately 900 nm), ultrafine grain (approximately 125 nm), and nano grain (approximately 35 nm) microconstituents resulted in a very high-compressive strength (approximately 1000 MPa) and acceptable strain-to-failure under high-strain rate loading (*1, 2*). Realization of such multiscale microstructure was possible because of the extreme nonequilibrium processing route of mechanical attrition of constituent powders in a cryogenic medium, called cryomilling. During cryomilling in such an extreme environment, e.g., at $-196\text{ }^{\circ}\text{C}$ with liquid nitrogen (LN₂) as the cryogenic medium, recrystallization of nanograins do not occur and hence the nanostructure is retained. It has also been observed that during attrition with liquid nitrogen, nitrides are formed in the grain boundaries. The nitride particles with particle size in the order of 15–20 nm act as dispersoids and directly enhance the strength of the composite by dispersion strengthening (*3, 4*) mechanism. Stearic acid is usually used as the process control agent (PCA) during cryomilling of aluminum alloys (*5*), which also introduce carbides into the powders providing additional strengthening. The nanodispersoids help in retaining the nanostructure of AA5083 by inhibiting grain growth during high-temperature thermo-mechanical processing of powders (necessary to produce bulk materials). AA5083 nanograins contribute significantly to overall strength of the MMC by a strengthening mechanism brought about by grain size refinement (*3, 4*).

In cryomilling, use of a PCA, as a surface active substance, is essential to prevent excessive cold welding of the powders. PCA introduces contaminants, slows down the milling process, and also alters the milling product (*6*). Once milling is completed, the PCA has to be removed to allow for a clean and strong interfacial bonding between the nanostructured particles during thermo-mechanical processing to transform the powders into bulk form. The removal process, known as degassing, is done by heating the powders at high temperature. The degassing process allows for the possibility of grain growth for the nanostructured aluminum and subsequent degradation of mechanical response of MMC. The temperature required for the degassing process is determined by the relative volatility of the PCA, therefore, the choice of PCA is very important. In this study, the effect of the PCA on the microstructure and resultant mechanical properties of the

consolidated composites was examined. Cryomilling was carried out with three different PCAs: caprylic acid, oleic acid, and stearic acid. The degassing temperatures were also varied to determine the optimal degassing parameters that would result in a composite of minimum impurity and maximum mechanical properties. The goal of the project is to optimize the cryomilling and degassing process in order to manufacture high-strength low-density aluminum composites for structural applications. In this report, preliminary results that demonstrate the process-dependent chemistry and properties are presented. Some physical and chemical properties of PCAs are listed in table 1. The carbon and hydrogen concentrations for the three acids are similar; however, caprylic acid has almost double the amount of oxygen.

Table 1. Physical and chemical properties of stearic, oleic, and caprylic acid (7).

	C (wt.%)	H (wt.%)	O (wt.%)	Boiling Point (°C)	Physical State at Room Temp
Stearic Acid	76	12.75	11.25	383	Waxy solid
Oleic Acid	76.54	12.13	11.33	286	Oil
Caprylic Acid	66.63	11.18	22.19	239.7	Oil

2. Experimental

A Szegvari Union Process 1-S attritor was modified to allow for continuous flow of LN2. Powders were cryomilled in LN2 for 8 h with a ball to powder weight-ratio of 32:1. AA5083 (–325 mesh from Valimet, Inc) and B₄C (Micro Abrasives Corporation) powders were blended in a V-blender for up to 24 h before cryomilling. To determine the effect of the PCA on the microstructure and mechanical properties, 0.25 wt.% of oleic, caprylic, or stearic acid was added to the powder to be cryomilled. Stearic acid was V-blended with the powder prior to cryomilling to ensure a uniform distribution of PCA. Oleic and caprylic acids are liquid at room temperature and could not be added directly to the blender; therefore, these acids were mixed with LN2 and added directly into the attritor.

After cryomilling, the powders were collected and placed in a glove box to allow for the LN2 to boil-off. To improve ductility of the composite, additional unmilled AA5083 powders were added to the cryomilled powders and V-blended for 24 h. The final composite consisted of 60 wt.% nanostructured AA5083, 10 wt.% B₄C, and 30 wt.% coarse grain AA5083. The powders were degassed between 275 and 410 °C in a custom-made static vacuum degasser with a maximum vacuum of approximately 10–6 torr. The degassing temperature for the powder containing stearic acid was 410 °C, which is above its boiling point. Once high vacuum was achieved, the furnace was ramped to the desired temperature over 6 h, soaked for 8 h, and then the heater was shut off, and allowed to cool to room temperature. Powder was consolidated

through cold isostatic pressing followed by high-strain rate extrusion, which was carried out on a Dynapak press with a reduction ratio of approximately 6:1. Table 2 summarizes the process variation of specimens examined in this study with sample designations.

The agglomerate size and distribution of the powders was observed with an Olympus LEXT OLS 3000 confocal optical microscope (OM). Scanning electron microscopy (SEM) was conducted on the as-cryomilled powders using a Zeiss ULTRA-55 field emission scanning electron microscope operating at 15 kV and 8 mm working distance to examine the microstructure of the as-cryomilled powders. Mechanical testing was conducted on the samples according to ASTM standard E9¹ for compression testing. The composition analysis for the hydrogen, nitrogen, and oxygen impurities in the consolidated samples were determined by inert gas fusion technique (Spectrographic Technologies, Pittsburgh, PA).

Table 2. Sample IDs along with the PCA used and degassing temperature.

Sample ID	S-410	O-310	C-275	O-410	C-410
PCA	0.25 wt.% stearic acid	0.25 wt.% oleic acid	0.25 wt.% caprylic acid	0.25 wt.% oleic acid	0.25 wt.% caprylic acid
Degassing Temp (°C)	410	310	275	410	410

3. Results and Discussion

3.1 Microstructure of Cryomilled Powders

Optical micrographs of the powders cryomilled for 8 h (prior to degassing) using oleic, caprylic, or stearic acid are shown in figure 1. They show similar microstructure regardless of the PCA used. Three types of agglomerates were identified in the powders: composite agglomerate (i.e., AA5083 and B₄C) with rounded shape (arrow 1 in figure 1c); circular, undeformed AA5083 agglomerate without B₄C (arrow 2 in figure 1c); and “pancake-shaped,” deformed aluminum agglomerates without B₄C (arrow 3 in figure 1d).

The powders are not homogeneous after 8 h of cryomilling. Inhomogeneous microstructure has been observed in other studies with similar milling conditions (8, 9). Cracks in the powder, as seen in figure 2, may be due to insufficient energy in the mill or too much PCA (limiting the cold welding of the agglomerates).

¹Standard Test Methods of Compression Testing of Metallic Materials at Room Temperature. Published 11/01/2009 by ASTM International.

It is expected that B_4C can assist in the cold fracturing of the powder during cryomilling and reduce the final grain size (10). Therefore, the grain size in the powder likely varies between the powder agglomerates with and without B_4C . It is important to note that although it is unlikely that the powders have a uniform grain size, it is expected that the three powders analyzed in this study have the same variation in grain size because they have similar types and distribution of agglomerates. Therefore, the overall contribution to strength by grain size is expected to be similar for all three powders.

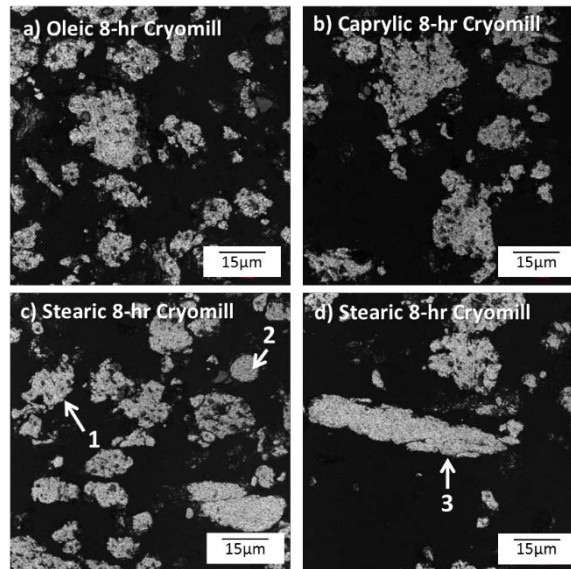


Figure 1. Optical micrographs of aluminum composite agglomerates after 8 h cryomilling with (a) oleic acid, (b) caprylic acid, and (c, d) stearic acid.

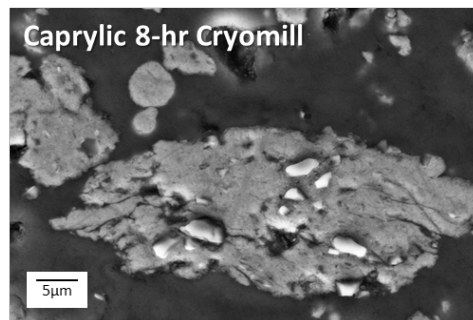


Figure 2. Secondary electron micrograph of the aluminum composite agglomerate after cryomilling with caprylic acid as the PCA.

3.2 Hydrogen, Oxygen, and Nitrogen Impurities

In figure 3, hydrogen concentration has been plotted as a function of degassing temperature. Hydrogen concentration decreases with an increase in degassing temperature. Hydrogen may be released from the powder in one of three ways: (1) through the removal of moisture from the powder, (2) from the reaction of absorbed moisture with the aluminum matrix, which produces alumina and hydrogen gas, and/or (3) from the decomposition of the PCA. At the highest degassing temperature, the removal of hydrogen is equally efficient regardless of the PCA chosen. Assuming that all of the powders had a similar absorbed moisture concentration before degassing and moisture is the primary degassing product, there would be a correlation between residual hydrogen and oxygen concentration in the sample. As presented in figure 4, no such correlation exists. On the other hand, assuming that the majority of the moisture reacts with the aluminum matrix to produce hydrogen gas, it would be expected that at the highest temperature, 410 °C, where the most hydrogen is removed from the sample, there would also be the highest amount of oxygen retained in the sample. Upon examining figure 4, this correlation is not observed either. Therefore, it may be suggested that both the degassing of moisture and the reaction of moisture with the aluminum matrix occurs.

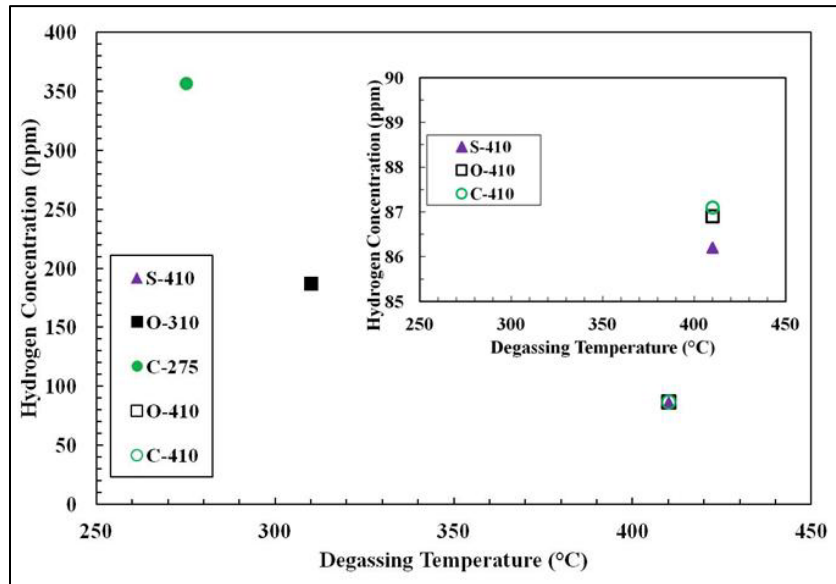


Figure 3. Hydrogen concentration vs. degassing temperature.

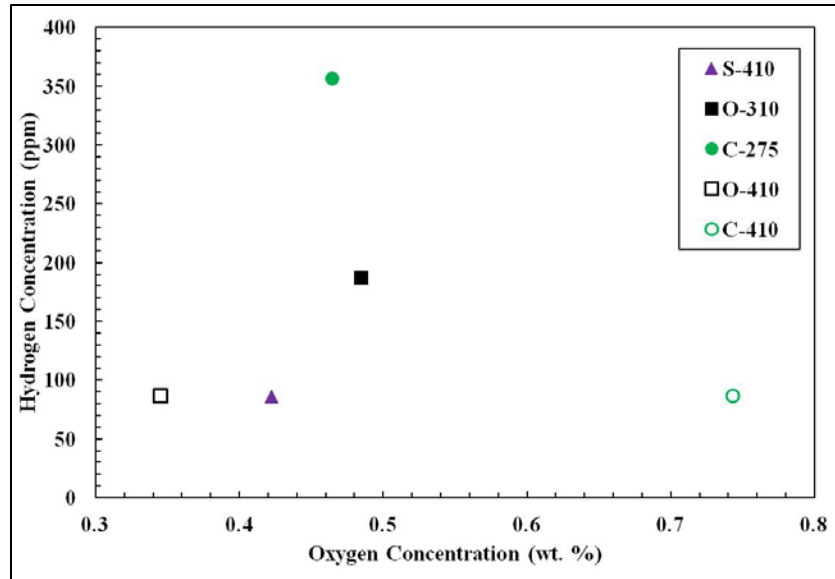


Figure 4. Hydrogen concentration vs. oxygen concentration.

Figure 5 shows that there is a clear correlation between the concentrations of oxygen and nitrogen. Similar results have been reported previously for aluminum composites reinforced with AN (11). This data suggests that the mechanism behind nitrogen storage is directly related to the oxygen retained in the sample.

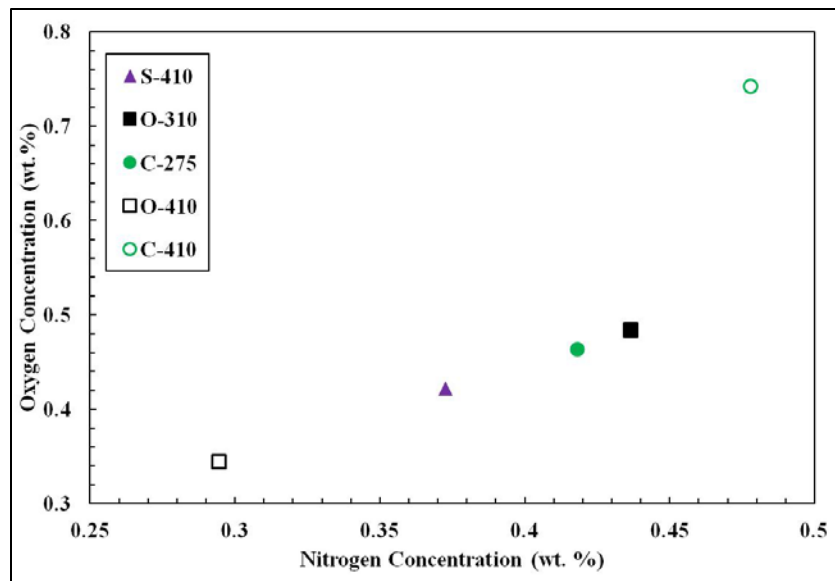


Figure 5. Oxygen concentration vs. nitrogen concentration.

If only the samples degassed at 410 °C were considered, it is clear that the choice of PCA affects the resultant oxygen and therefore the nitrogen content. Recall that the concentration of oxygen is similar in oleic and stearic acids but much less than that of caprylic acid. Therefore, it is logical that there would be higher oxygen impurity in the powder treated with caprylic acid. However, if the C-275 and C-410 are considered (both cryomilled with caprylic acid) but degassed at 275 and 410 °C, respectively, it is obvious that the choice of degassing temperature is also critical in controlling the final oxygen and nitrogen concentrations.

3.3 Compressive Strength

In figure 6, compressive strength has been plotted against hydrogen concentrations of the samples. It shows that strength decreases with an increase in hydrogen concentration. For the most part, the mechanical properties are similar regardless of PCA chosen.

As shown in figure 3 the composite produced from C-275 powder contains a very high-hydrogen content as compared to the other composites tested. In figures 7 and 8, this composite shows a low strength, but it would be unreasonable to conclude that this is a result of the nitrogen or oxygen concentrations in the sample. Therefore, when discussing the trend in strength with nitrogen and oxygen this data point is ignored. As a result, it is observed that the increases in oxygen and nitrogen concentration (as presented in figure 7 and 8, respectively) results in a slight increase in compressive strength.

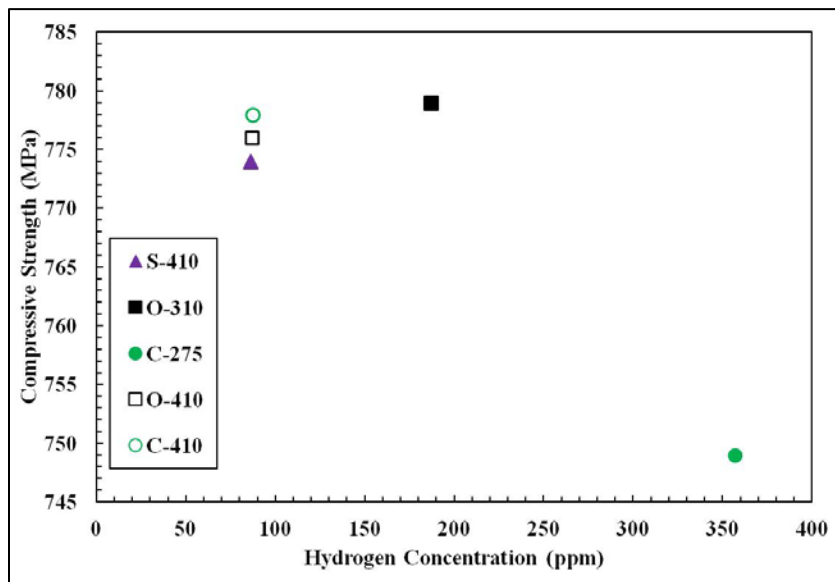


Figure 6. Compression strength vs. hydrogen concentration.

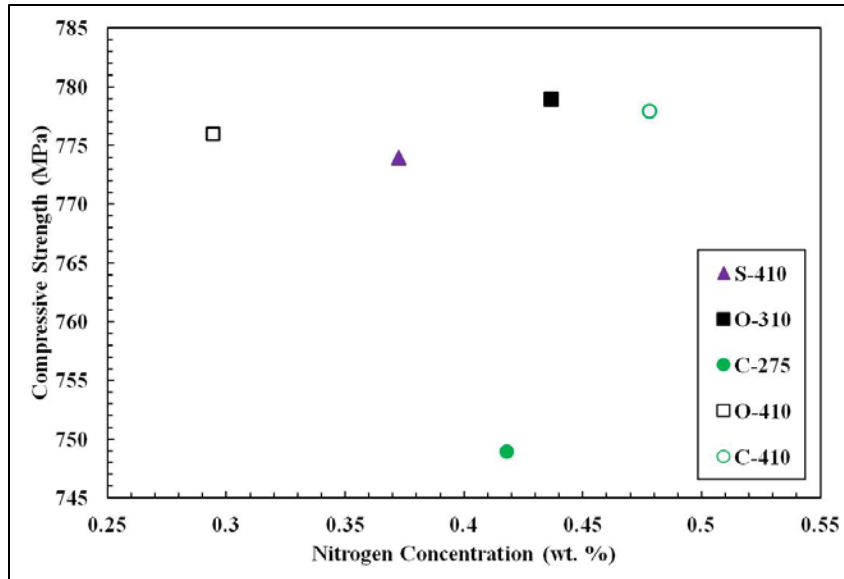


Figure 7. Compressive strength vs. oxygen concentration.

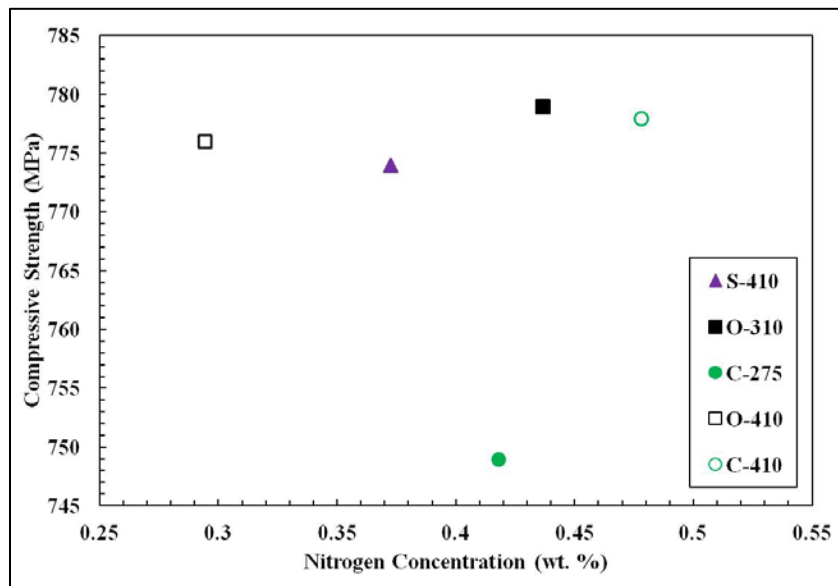


Figure 8. Compressive strength vs. nitrogen concentration.

4. Conclusions

Chemistry, microstructure, and compressive strength of B₄C reinforced AA5083 composites were examined with respect to impurity content arising from cryomilling in liquid nitrogen. Microstructure of the as-cryomilled powders was similar regardless of the PCA used. Hydrogen content decreased with increasing temperature of degas anneal. A clear correlation between oxygen and nitrogen content was also observed. A slight increase in the compressive strength was observed with increases in oxygen and nitrogen concentrations. However, excessive hydrogen content had a strong deleterious influence on the composite compressive strength. Tensile tests are being carried out to determine the influence of hydrogen, oxygen, and nitrogen on tensile properties. A correlation between compressive and tensile properties is also being investigated in light of the impurity content that will be published elsewhere soon.

5. References

1. Zhang, H. T.; Ye, J. C.; Joshi, S. P.; Schoenung, J. M.; Chin, E. S. C.; Gazonas, G. A.; Ramesh, K. T. Superlightweight Nanoengineered Aluminum for Strength Under Impact. *Adv. Engg. Mater.* **2007**, 9, 355.
2. Ye, J.; Han, B. Q.; Lee, Z.; Ahn, B.; Nutt, S. R.; Schoenung, J. M. A Tri-Modal Aluminum Based Composite with Super-High Strength. *Scripta Mater.* **2005**, 53, 481.
3. Li, Y.; Liu, W.; Ortalan, V.; Li, W. F.; Zhang, Z.; Vogt, R.; Browning, N. D.; Lavernia, E. J.; Schoenung, J. M. HRTEM and EELS Study of Aluminum Nitride in Nanostructured Al 5083/B4C Processed via Cryomilling. *Acta Mater.* **2010**, 58, 1732.
4. Hofmeister, C.; Yao, B.; Sohn, Y. H.; Delahanty, T.; van den Bergh, M.; Cho, K. Composition and Structure of Nitrogen-Containing Dispersoids in Trimodal Aluminum Metal–Matrix Composites. *J. Mater. Sci.* **2010**, 45, 4871.
5. Witkin, D. B.; Lavernia, E. J. Synthesis and Mechanical Behavior of Nanostructured Materials via Cryomilling. *Prog. in Mater. Sci.* **2006**, 51, 1.
6. Shaw, L.; Zawrah, M.; Villegas, J.; Luo, H.; Miracle, D. Effects of Process-Control Agents on Mechanical Alloying of Nanostructured Aluminum Alloys. *Metallurg. Mater. Trans. A* **2003**, 34A, 159.
7. O’Neil, M. J.; Ed. *The Merck Index*; 13th Edition; Merck Research Laboratories: Whitehouse Station, NJ, 2001.
8. Liao, X. Z.; Huang, Y. J.; Zhu, Y. T.; Zhou, F.; Lavernia, E. J. Nanostructures and Deformation Mechanisms in a Cryogenically Ball-Milled Al-Mg Alloy. *Phil. Mag.* **2003**, 83, 3065.
9. Zhou, F.; Nutt, S. R.; Bampton, C. C.; Lavernia, E. J. Nanostructure in an Al-Mg-Sc Alloy Processed by Low-Energy Ball Milling at Cryogenic Temperature. *Metallurg. Mater. Trans. A* **2003**, 34A, 1985.
10. Kamrani, S.; Riedel, R.; Reihani, S. M. S.; Kleebe, H. J. Effect of Reinforcement Volume Fraction on the Mechanical Properties of Al–SiC Nanocomposites Produced by Mechanical Alloying and Consolidation. *J. Composite Mater.* **2009**, 44, 313.
11. Goujon, C.; Goeuriot, P.; Delcroix, P.; Le Caer, G. Mechanical Alloying During Cryomilling of a 5000 Al Alloy/AlN Powder: the Effect Of Contamination. *J. Alloys Comp.* **2001**, 315, 276.

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